

AD-A180 314 PREPARATION AND PROPERTIES OF CUBIC ZRO2 STABILIZED
WITH Ni(II)(U) BROWN UNIV PROVIDENCE RI DEPT OF
CHEMISTRY K E SMITH ET AL 15 MAY 87 TR-5 1/1

UNCLASSIFIED

N08814-86-K-0234

F/G 7/4

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AD-A180 314

OFFICE OF NAVAL RESEARCH
CONTRACT NO. N000 14 86K0234
TECHNICAL REPORT No. 5

(12)

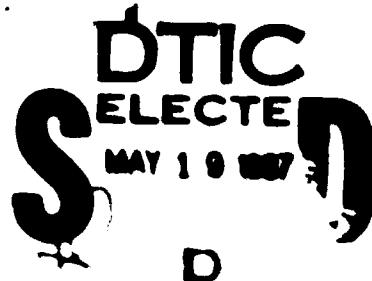
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PREPARATION AND PROPERTIES OF CUBIC ZrO₂ STABILIZED WITH Ni(II)

by

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Prepared for publication
in
MATERIALS RESEARCH BULLETIN



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May 15, 1987

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION AVAILABILITY OF REPORT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			
4 PERFORMING ORGANIZATION REPORT NUMBER(S) OS		5 MONITORING ORGANIZATION REPORT NUMBER(S) NOOO 14 86K0234	
6a NAME OF PERFORMING ORGANIZATION AARON HOLD BROWN UNIVERSITY	6b OFFICE SYMBOL (if applicable)	7a NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH DR. DAVID NELSON	
7b ADDRESS-CITY STATE AND ZIP CODE CHEMISTRY DEPT. BOX D PROVIDENCE, RI 02912		7b ADDRESS-CITY STATE AND ZIP CODE CODE 472 800 N. QUINCY STREET ARLINGTON, VA 22217	
8a SOURCE OF FUNDING AGENCY NSF	8b SOURCE OF FUNDING (if applicable)	9a FEDERAL INSTRUMENT IDENTIFICATION NUMBER	
9b SOURCE OF FUNDING AGENCY		10a PROJECT NUMBER	
		PROJECT NO.	10b TASK NO.
		10c WORK UNIT NO.	10d SUBCONTRACTOR NO.
<p align="center">11. SUBJECT OF INVESTIGATION</p> <p align="center">PREPARATION AND PROPERTIES OF CUBIC ZrO₂ STABILIZED WITH Ni(II)</p>			
<p align="center">K.E. Smith, R. Kershaw, K. Dwight and A. Hold</p>			
12a TYPE OF REPORT Technical	12b DATE OF REPORT May 11, 1987	14. DATE OF REPORT (Year Month Day)	15. SPONSORING ACTIVITIES

SUBMITTED FOR PUBLICATION IN MATERIALS RESEARCH BULLETIN

13. NAME OF AUTHOR K. E. Smith, R. Kershaw, K. Dwight, A. Hold	16. SUBJECT TERMS (List one or more terms or phrases in reverse of necessary and desired by part number) Nickel nitrate, nickel oxide, zirconyl nitrate, zirconium oxide
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Preparation and Properties of Cubic ZrO₂ Stabilized with Ni(II)

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ABSTRACT

Samples of cubic stabilized ZrO₂ have been prepared by the codecomposition of nickel nitrate and zirconyl nitrate at 500°C. A comparison of the stability towards reduction of the bulk NiO and the Ni(II) in the cubic stabilized ZrO₂ demonstrates the influence of the stabilization of cubic ZrO₂ with Ni(II).

MATERIALS INDEX: Nickel nitrate, Nickel oxide, Zirconyl nitrate, Zirconium oxide.

Introduction

Nickel oxide has been studied on a variety of support materials such as Al₂O₃ (1, 2), ZrO₂ (2), MgO (3), TiO₂ (3), and SiO₂ (4). The Fischer-Tropsch activity of the nickel-zirconia system has been investigated and preparations of the catalyst involving coprecipitation gave a significantly more active catalyst than did preparations involving impregnation (5). Stabilization towards reduction has been observed when certain transition metal ions such as Rh(III) are inserted into the fluorite ZrO₂ structure (6). Recent investigations using the NiO/ZrO₂ system have concluded that NiO does not interact with ZrO₂, but the materials were prepared by incipient wetness (7).

It was the purpose of this study to investigate the formation of cubic ZrO₂ stabilized with Ni(II) and to relate the structural properties of the catalyst with its observed stability in reducing atmospheres. These properties were then compared to those of catalysts prepared by incipient wetness. Changes in the structure of ZrO₂ and in the temperatures at which reduction of Ni(II) to Ni metal occurred were then related to the relative strengths of the catalyst-support interaction.

Experimental

Samples of cubic ZrO₂ stabilized with Ni(II) were prepared to give compositions ranging between 10 and 30 mole percent calculated as NiO. The desired quantities of Ni(NO₃)₂·6H₂O (Aesar 99.7%, lot 011783) and ZrO(NO₃)₂ (8) were dissolved in distilled water. Ten ml of water were added for each gram of ZrO(NO₃)₂. The molecular weights of Ni(NO₃)₂·6H₂O and ZrO(NO₃)₂ were determined by thermogravimetric analysis and found to be 298 and 245 respectively, compared to the calculated values of 291 and 231. The differences between the experimental and theoretical values are due to the hygroscopic nature of the

nic +1 nitrate and adsorbed water on the zirconyl nitrate. The solutions were then dried at 150°C for 24 hours, ground in an agate mortar and heated in air at 500°C for 34 hours. Bulk $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the double salt of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2$ were dissolved in distilled water and dried at 150°C for 24 hours. The material resulting from this drying was decomposed in a thermogravimetric balance under a predried flowing oxygen atmosphere with a flow rate of 30 ml/minute. The samples were heated to 700°C at a rate of 100°C/hour.

Samples prepared by incipient wetness were obtained by drying an aqueous slurry of tetragonal ZrO_2 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 150°C for 24 hours. The resulting material was then ground in an agate mortar and decomposed in air at 500°C for 34 hours. This temperature was chosen to facilitate the comparison between these samples and those prepared by codecomposition.

The temperature programmed reductions of bulk NiO as well as samples containing calculated values of 10, 16 and 30 mole percent of NiO were carried out in a thermogravimetric balance. These reductions were also studied on a thermogravimagnetic balance (9). The resulting data gives two kinds of information: first, the normal thermogravimetric data is obtained (loss of weight as a function of temperature) and second, the oscillating weight changes are obtained which reflect the field on and field off environment of the sample. For example, as antiferromagnetic NiO is reduced to ferromagnetic Ni metal, the oscillating signal from the magnet increases until the Curie temperature is reached and then decreases again.

Characterization of Products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405\text{\AA}$). The diffraction patterns were taken in the range of $12^\circ < 2\theta < 72^\circ$ with a scan rate of $1^\circ 2\theta/\text{minute}$ and a chart speed of 30 inches/minute.

The temperature programmed reductions were performed in a Cahn System 113 thermal balance. The heating rate was 30°C/hour up to 950°C in an atmosphere of a predried 85%Ar/15% H_2 mixture.

The thermogravimagnetic studies were performed in a balance which was designed and built in our laboratory (9). This balance incorporates a Cahn RG electrobalance and has a pivoted permanent magnet that sweeps through the area surrounding the sample bucket at a rate of one revolution per minute.

The magnetic measurements were performed on the Faraday balanced described by Morris and Nold (10). The susceptibility was measured from 77 K to room temperature and was corrected for the theoretical core diamagnetism.

Results and Discussion

Samples of $\text{Ni(II)}/\text{ZrO}_2$ were prepared by double decomposition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2$. The temperature programmed decompositions of both bulk nickel nitrate and bulk zirconyl nitrate, as well as the double salt of nickel and zirconyl nitrates, were carried out in order to compare their

decomposition temperatures. Pure nickel nitrate decomposes to the oxide at 320 \pm 15°C. This is in agreement with results reported by Weigel et al. (11). The final product was gray and gave an x-ray pattern that corresponded to cubic NiO. Decomposition of zirconyl nitrate at 500°C in air for 4 hours showed predominantly tetragonal ZrO_2 with a small amount of the monoclinic phase. With prolonged heating (34 hours) of the sample, the observed amount of the monoclinic phase continued to increase. With a rate of heating of 100°C/hour, the decomposition of the corresponding double salt was observed to be essentially complete by 500°C, and therefore this temperature was chosen for the decomposition of the double salts.

A sample of the double salt was prepared such that the resulting decomposition would give 10 atomic percent Ni(II)/ ZrO_2 . X-ray patterns of the products taken after 4 hours and after 34 hours at 500°C (in air) were identical and showed cubic ZrO_2 . The lack of additional decomposition during the longer heating period suggests that complete decomposition was obtained. Fig. 1 shows

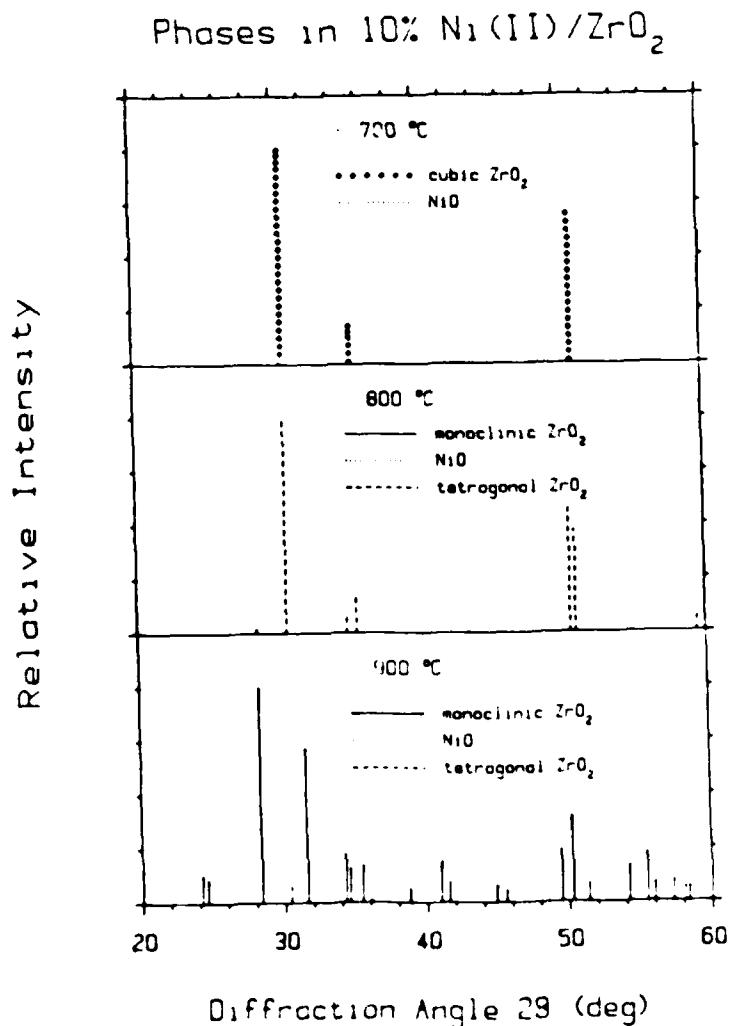


Fig. 1. Phase analysis as a function of temperature for 10 atomic percent Ni(II) in ZrO_2

that the stabilized cubic phase of ZrO_2 containing 10 atomic percent Ni(II) persists below 800°C. At 800°C the tetragonal phase predominates. By 900°C the phase is essentially all monoclinic and the (012) and (101) peaks of NiO are now much more intense. This indicates that the Ni(II) is no longer in solid solution with ZrO_2 .

When the introduction of Ni(II) was attempted through incipient wetness techniques, no stabilization of the cubic ZrO_2 was observed. For such samples prepared at 500°C, both the tetragonal and monoclinic phases were observed although the tetragonal peaks at 50.2° were not clearly resolved (Fig. 2). The NiO peaks (012 and 101) were clearly evident. These results suggest that codecomposition of the nitrates is the method of choice to obtain a solid solution of Ni(II) in ZrO_2 .

Phases in 16% Ni(II)/ ZrO_2

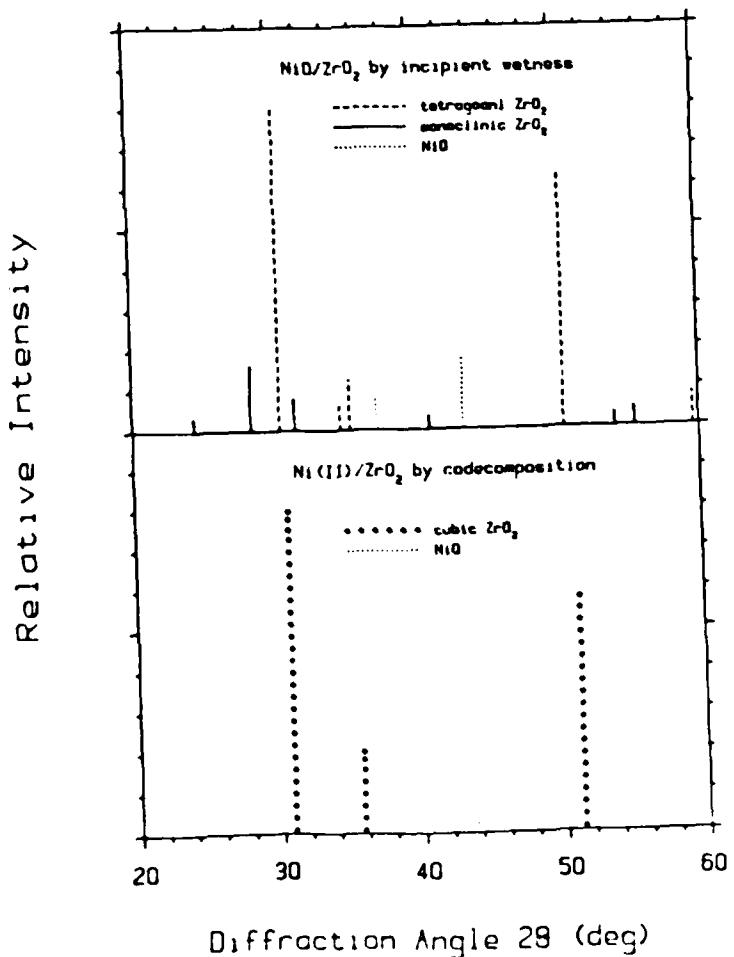


Fig. 2. Phase analysis of samples of 16 atomic percent NiO/ ZrO_2 , (incipient wetness), and Ni(II)/ ZrO_2 (codecomposition) prepared at 500°C.

From x-ray analysis it was determined that products of the cubic stabilized ZrO_2 prepared at 500°C were single phase up to a concentration of approximately 16 atomic percent Ni(II). Samples containing more than 16 atomic percent Ni(II) showed the presence of bulk NiO as indicated by x-ray analysis. The thermogravimagnetic data for the 16 atomic percent sample in a reducing atmosphere shows that the signal from the magnet begins to increase at 310°C and concurrently the weight begins to decrease. This demonstrates that the decrease in weight corresponds to the appearance of Ni particles. Therefore, the reduction of Ni(II) to Ni metal may be followed either as a function of weight loss or by growth of the signal resulting from the formation of a magnetic phase (Ni).

Under the same conditions, a 10 atomic percent Ni(II) sample shows no magnetic signal or weight loss at 310°C. In fact, no Ni metal was detected as the temperature was raised up to the Curie temperature (358°C). Therefore, the maximum amount of Ni(II) that can form solid solution with ZrO_2 is between 10 and 16 atomic percent Ni(II). It can be seen in Fig. 3 that, for the sample containing 10 atomic percent Ni(II), only one reduction step is observed, which is due to the reduction of Ni(II) in the ZrO_2 . For samples with 16 atomic percent Ni(II) and higher, two reductions are observed. The reduction at the lower temperature is due to bulk NiO; that at the higher temperature is due to reduction of Ni(II) present in the ZrO_2 .

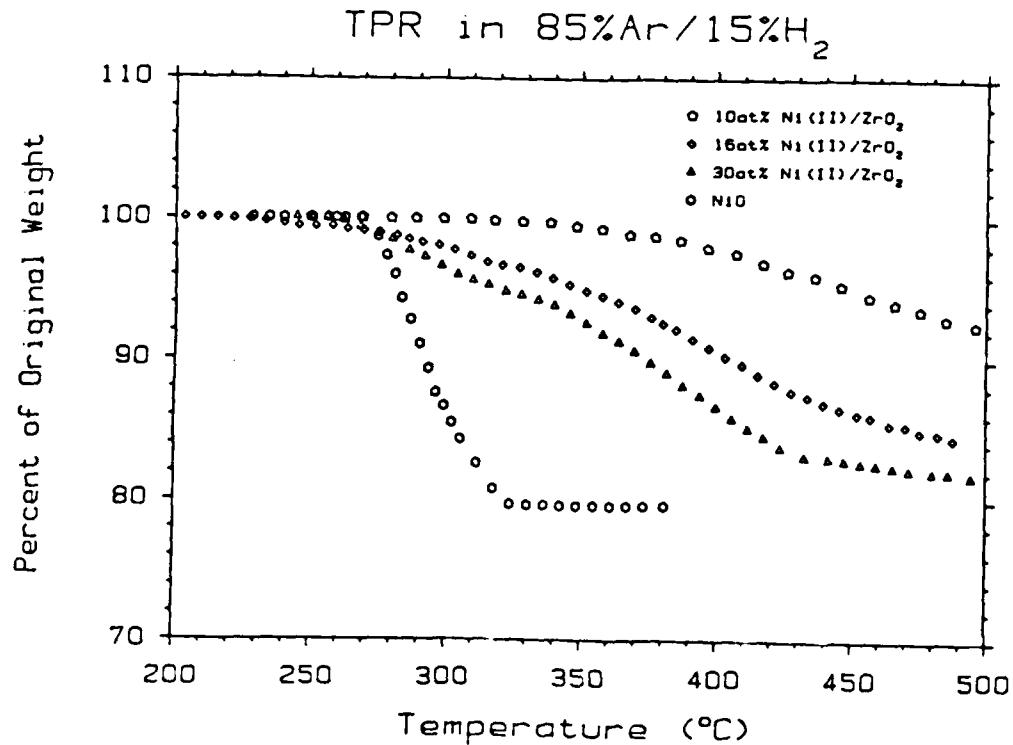


Fig. 3. Temperature programmed reduction in 85%Ar/15%H₂ of Ni(II)/ ZrO_2 and NiO

Bulk NiO prepared from the nitrate and decomposed at 500°C shows antiferromagnetic behavior. However, the temperature dependence of the magnetic susceptibility of the Ni(II) in solid solution with ZrO₂ shows paramagnetic behavior with weak antiferromagnetic interactions and a moment of 3.1 BM. Interpretation of the deviation from the spin-only moment of 2.8BM would be dependent on the coordination of the Ni(II) in the fluorite structure. Preliminary results suggest that it is possible to have a first row transition metal in 8-fold coordination (Zr sites or in the equivalent site found in the central cavity of the fluorite cubic cell).

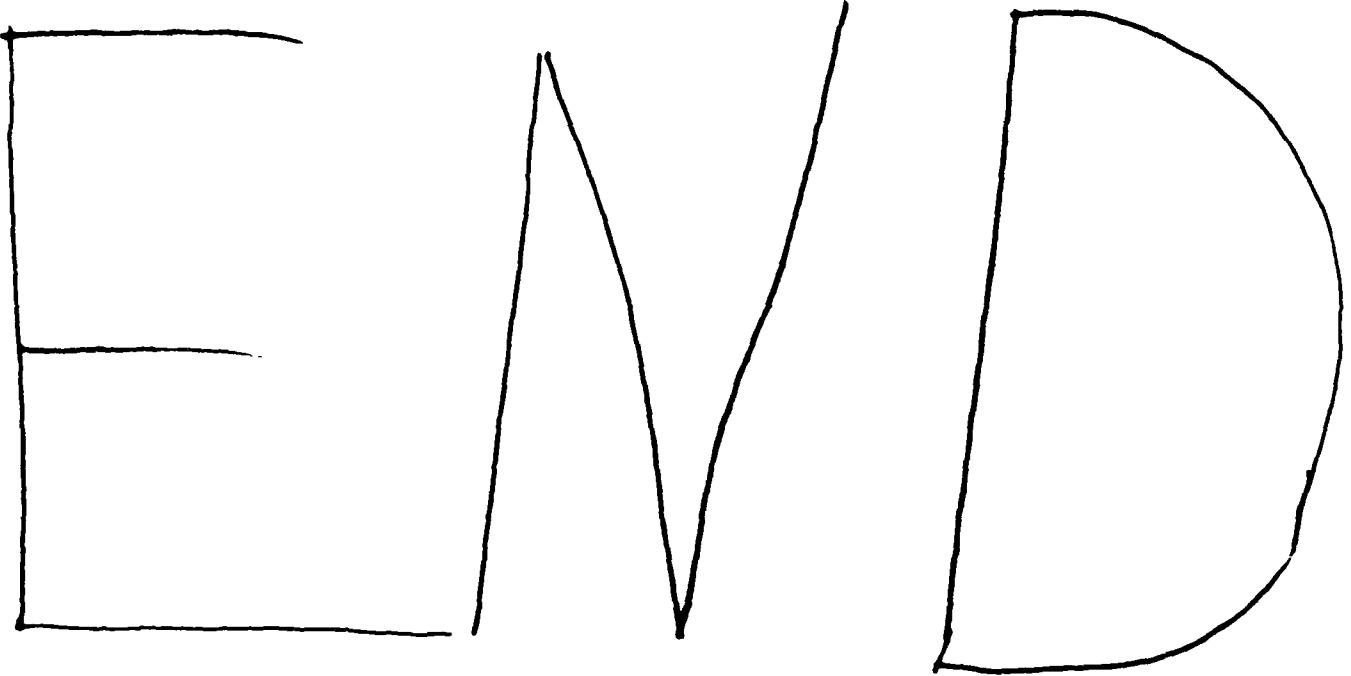
Acknowledgments

This work was supported in part by the Eastman Kodak Company and the Office of Naval Research. In addition, acknowledgment is made to the National Science Foundation, Grant No. DMR-820-3667, for the partial support of K. Dwight. The authors also express their appreciation for the use of Brown University's Materials Research Laboratory which is supported by the National Science Foundation.

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